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THE CRYSTAL STRUCTURE OF STRONTIUM BROMIDE

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In 1939, Döll and Klemm[1] published a powder X-ray diffraction diagram

(1) W. Döll and W. Klemm, Z. Anorg. Chem., 241, 239 (1939).

for strontium bromide. These authors were unable to give any interpretation of the diagram except that it appeared to be qualitatively similar to those of europium bromide and samarium bromide. A single crystal X-ray diffraction investigation of the structure of strontium bromide was reported in 1939 by Kamermans[2]. The assigned structure is a distorted version of

(2) M. A. Kamermans, Zeit. Krist., 101, 406 (1939).

the lead chloride structure. The space group is D_{2h}^{16} - Pbnm (Pnma) with a = 9.20 Å, b = 11.42 Å and c = 4.3 Å. The structure is quite an open one with most of the nearest strontium-bromine distances considerably longer than the sum of the ionic radii. Also it was observed that the structure proposed by Kamermans did not fit the powder pattern presented by Döll and Klemm. In an attempt to clarify the structural properties of strontium bromide this paper describes a reinvestigation of the crystalline state by the method of powder X-ray diffraction techniques.

A sample of hydrated strontium bromide was heated in vacuum at 200°C for several hours. A flat powder sample of the resulting anhydrous material was prepared in a dry box and transferred in a desiccator to the X-ray

diffractometer. The diffractometer radiation shield was covered by a polyethylene envelope enclosing both sample and a silica gel desiccant. All diffraction data were recorded on an automatic recording powder diffractometer equipped with a geiger counter detector. The resulting diffraction pattern was indexed on the basis of a tetragonal cell with

$$a = 11.633 \pm 0.009 \text{ Å}$$

$$c = 7.155 \pm 0.008 \text{ Å}$$

$$(CuK\alpha_1 = 1.5405 \text{ Å}).$$

The observed systematic absences

$$hk0;\ h + k = 1 \pmod 2$$

are consistent with space group $D_{4h}^7 - P\frac{4}{n}mm$ or $C_{4h}^3 - P\frac{4}{n}$. Density measurements are consistent with ten molecular units per cell. This structure is in good agreement with the pattern pictured by Döll and Klemm. It thus appears that $SrBr_2$, $EuBr_2$ and $SmBr_2$ are all isostructural tetragonal structures.

A sample of hydrated strontium bromide was kept in vacuum at room temperature for several hours. A powder X-ray diffraction pattern of the resulting material showed it to consist of a single phase with an orthorhombic unit cell identical to that reported by Kamermans. A weighed sample of this material was then heated in vacuum at 200°C for several more hours. An X-ray diffraction pattern of the resulting material showed it to be completely transformed into the tetragonal structure. A weight loss was observed during the heating which corresponds to one mole of water per mole

of resulting anhydrous strontium bromide. It thus seems that the single crystals Kamermans had were actually $SrBr_2 \cdot H_2O$.

We are at present investigating the structure of this monohydrate by single crystal techniques.

Sets of relative intensities were obtained for the various diffraction peaks of the anhydrous material by taking the height of the peak times its half width as a measure of its area and correcting for the angular factors in the usual way. Several attempts were made to find a suitable set of atomic parameters based on the space group D_{4h}^7 - $P\frac{4}{n}mm$. These all proved unsuccessful. A solution based on the space group D_{4h}^3 - $P\frac{4}{n}$ seemed necessary but also awkward because $|F_{hkl}| \neq |F_{h\bar{k}l}|$ thereby making almost every peak unresolved. At this point an extensive literature search revealed two other compounds of the type AB_2 which crystallize in a tetragonal cell with 10 formula units/cell; α-US_2[3] and α-USe_2[4]. No space group or structural

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(3) M. Picon and J. Flahaut, Comptes rendus, 237, 1160 (1953).

(4) P. Khodadad, Bull. Soc. Chim., p. 133 (1961).

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information is given in the literature, but Slater[5] observes that α-US_2

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(5) R. C. L. Slater, private communication (1963).

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crystallizes in space group

C_{40}^{10} - I4cm with

$$a = 10.26 \text{ Å}$$

$$c = 6.315 \text{ Å} .$$

If one assumes that $SrBr_2$ and α-US_2 are actually isostructural and that the apparent difference in the space groups is due to the anion contribution (which is difficult to observe in the α-US_2 data), the uranium parameters assigned by Slater can be used as trial parameters for the strontium atoms. Following this scheme, the approximate bromine atom positions have been deduced. By studying the variation of intensity of several reflections with changes in these parameters a structure consistent with the observed data was finally obtained. The atomic parameters are listed in Table 1. These parameters are referred to the origin at $\bar{1}$ at 1/4 1/4 o from $\bar{4}$. The atoms Sr_2 and Sr_3 are statistically distributed, one each in two-fold positions. The observed and calculated intensities of the various peaks are presented in Table 2. The notation hkl refers to both hkl and $h\bar{k}l$. The resulting structure is reasonable. Strontium atom type one has eight nearest bromine neighbors; one at 3.03 Å, three at 3.08 Å, two at 3.18 Å, one at 3.41 Å and one at 3.48 Å. Strontium atom type two has eight nearest bromine neighbors, all at 3.20 Å. The shortest bromine-bromine contact is between the two atoms Br_3 and Br_4 in special positions, namely 3.58 Å. The other nearest bromine-bromine contacts are at 3.78 Å, 3.98 Å, 4.02 Å and 4.15 Å.

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Table 1, $SrBr_2$ Atomic Parameters

Atom	Number and Position Notation	x	y	z
Sr_1	8g	0.088	0.588	0.245
$\frac{Sr_2}{2}$	2c	1/4	1/4	0.360
$\frac{Sr_3}{2}$	2c	1/4	1/4	0.860
Br_1	8g	0.155	0.460	0.604
Br_2	8g	0.345	0.460	0.115
Br_3	2a	1/4	3/4	0
Br_4	2b	1/4	3/4	1/2

Table 2, Observed and Calculated Intensities of $SrBr_2$

hkl	I_{obs}	I_{calc}	hkl	I_{obs}	I_{calc}
100	u	0	203	u	<1
110	1	<1	332 511 213	63	64
001	<1	<1			
101	1	<1			
200	<1	<1	520	u	0
111	1	<1	422	5	5
210	u	0	521 223	38	31
201	1	<1			
211	11	7	440	u	<1
220	1	1	303	1	<1
300	u	0	313 530	20	19
310	2	3			
002 221	1	<1	441	u	0
			502	u	1
102 301	15	16	432	u	<1
			600	7	5
112 311	41	55	512	u	1
			531	u	1
320	u	0	323 610	29	27
202	14	15			
212 321 400	59	65	601	u	0
			522 611 403 620	53	50
410	u	0			
330	8	9	413	5	2
222 401	2	<1	540	u	0
			333	u	0
302 411	87	109	004	u	1
			621 442	22	21
420	68	71			
312 331	66	58	104 541 423	17	18
421	30	29			
322 003	8	4	114 532 630	41	44
103	1	<1			
500	u	0	204 602	5	8
430	u	0			
113	u	0	214 612 631	17	12
510	u	<1			
402	25	19			
412 501 431	5	4	503 433	u	1

(Table 2, Continued)

hkl	I_{obs}	I_{calc}
700	u	0
513	100	101
710		
550		
224		
622		
304	45	50
542		
701		
640	5	5
314		
711	32	23
551		
523		
720	u	0
641	3	1
324	u	<1
632	14	5
721		
443	u	0
730	18	11
404		
414	u	2
702	44	32
334	89	75
552		
712		
731		
613		
650	u	0
424	33	20
642		